

***In Situ* Spectroscopy of Solvothermal Synthesis of Next- Generation Cathode Materials**

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BAT #183

Overview

Timeline

- Start date: Oct., 2018
- End date: Oct., 2021
- Percent complete: 30%

Budget

- Total project funding
 - DOE 100%
- Funding received (*FY19*)
 - 490 K

Barriers

- Barriers addressed
 - Low energy density
 - Cost
 - Cycle life

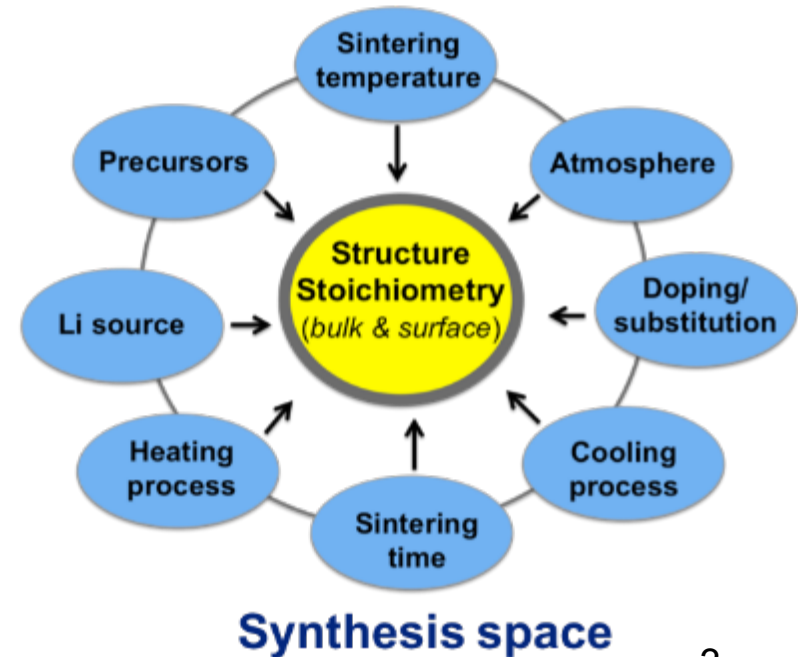
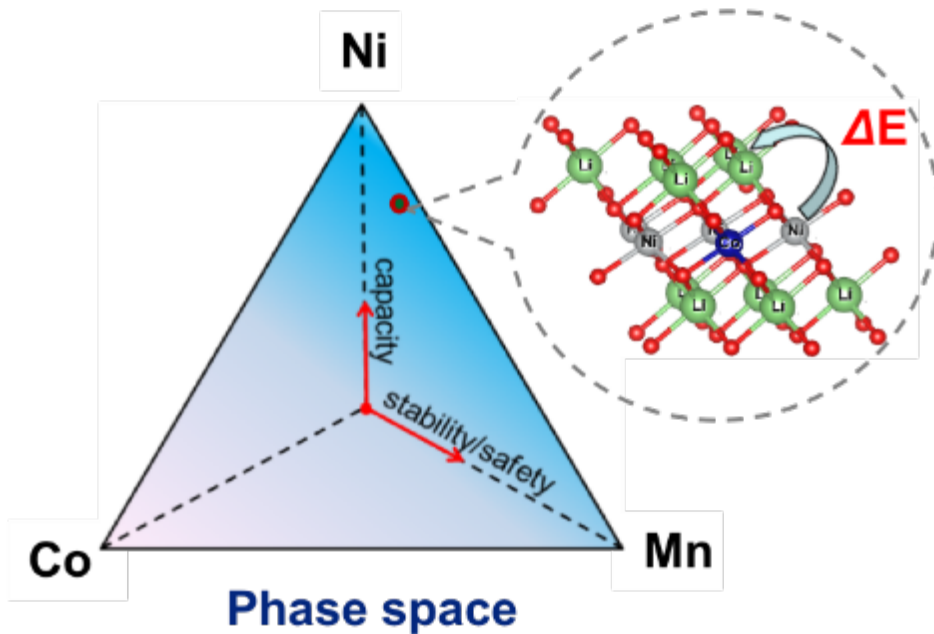
Partners

- Argonne National Lab
 - Materials synthesis
 - Characterization, modeling
- Lawrence Berkeley National Lab
 - Combined experimental/theoretical studies
- Oak Ridge National Lab
 - Neutron characterization
- Stony Brook University
 - Synchrotron and electron microscopy characterization
- Project lead: Brookhaven National Lab

Relevance and Objectives

Develop protocols for synthesis of next-generation cathode materials for lithium-ion batteries, with a focus on high-Ni NMC ($\text{LiNi}_x(\text{MnCo})_{1-x}\text{O}_2$; $x \geq 0.7$).

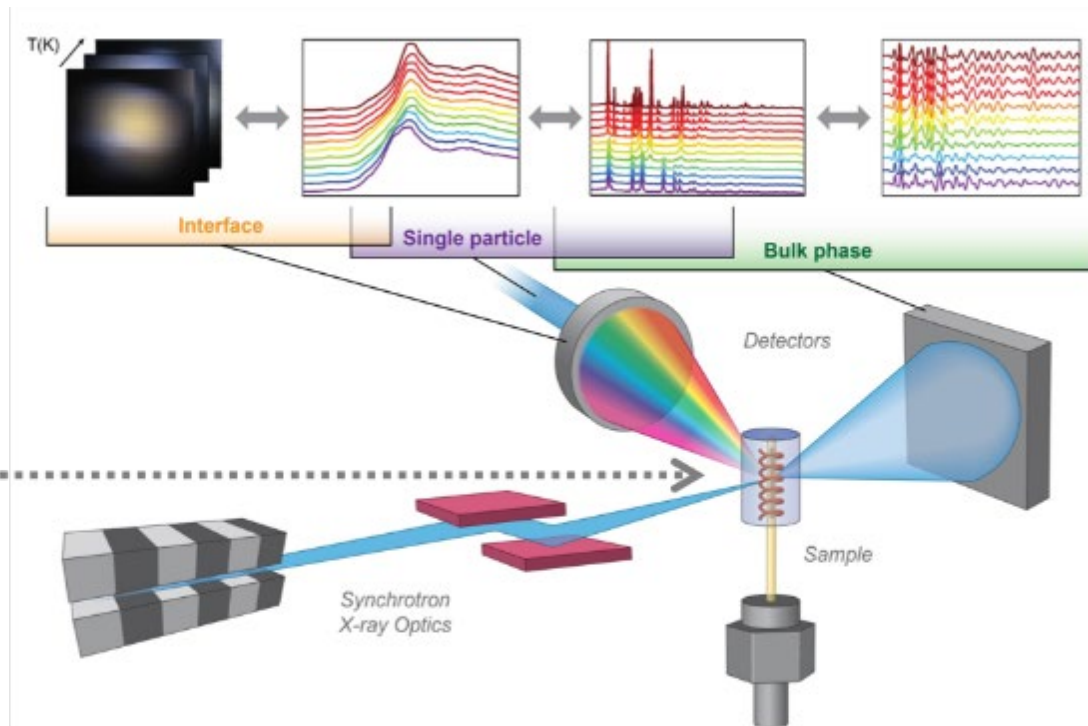
- **Electrode performance, which is largely determined by the structural properties of active materials, can be advanced by**
 - synthesis of *phase-pure* materials, and
 - control of their stoichiometry, morphology, surface/interfaces



Approach: *Synthesis by Design*



“black box”



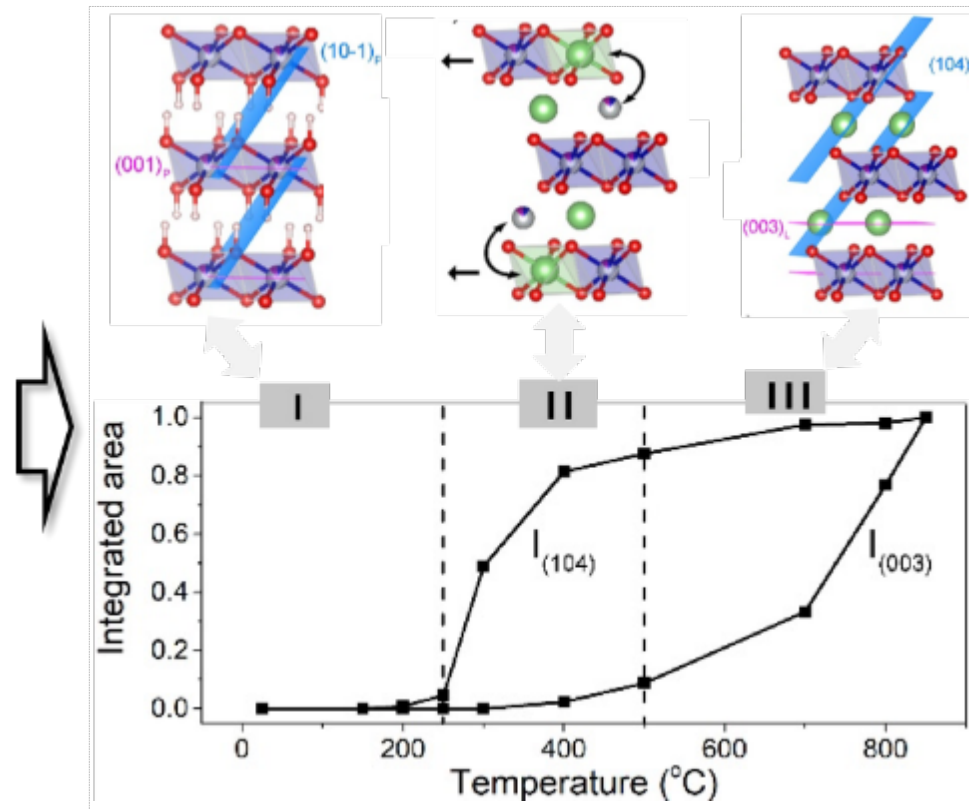
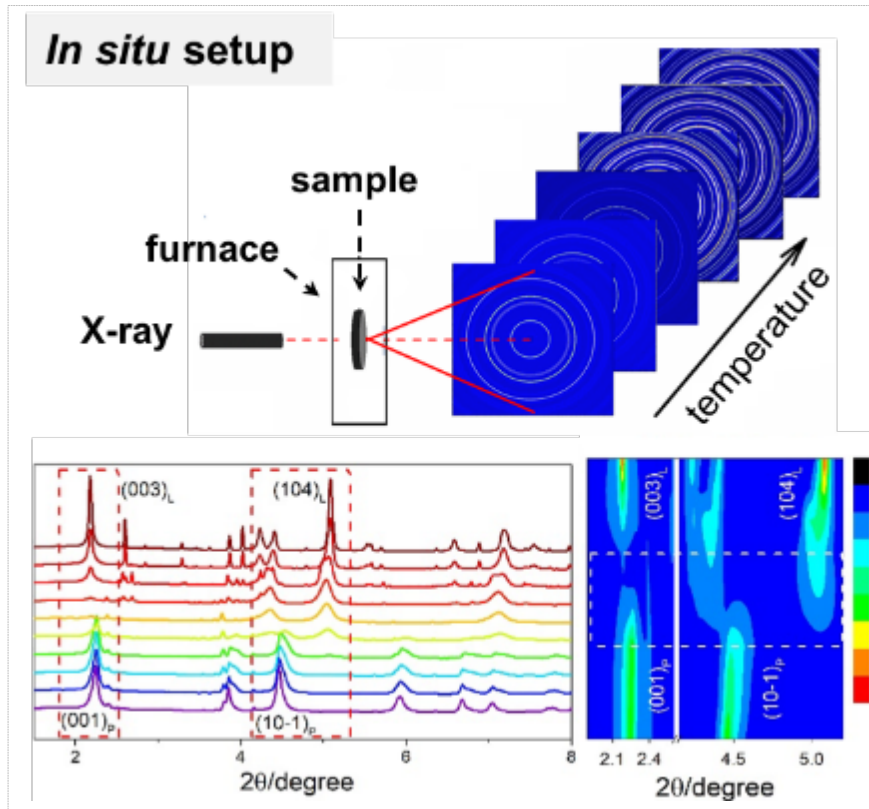
In situ reactor

- ***Synthesis by design***, aided by *in situ* studies of synthesis reaction
- explore the phase space under the real synthesis conditions, to identify intermediates/kinetic reaction pathways
 - quantify thermodynamic/kinetic parameters governing synthesis process (➔ *input for theory/modeling*)

Milestones

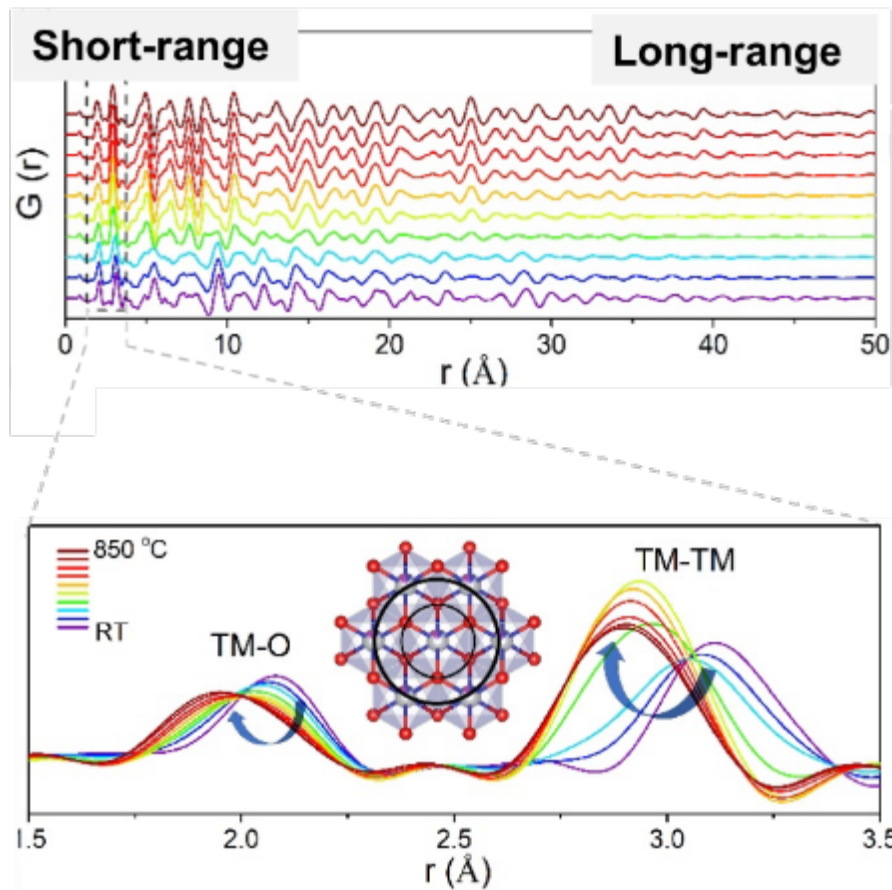
Time	Description (<i>status</i>)
Dec., 2018	Complete <i>in situ</i> studies of the local cationic ordering during solid-state synthesis of high-Ni NMC layered oxides from the hydroxide counterparts. (<i>complete</i>)
March, 2019	Identify the roles of Co/Mn substitution in tuning Li/Ni mixing in high-Ni NMC layered oxides. (<i>complete</i>)
June, 2019	Develop procedures for <i>in situ</i> probing and synthetic control of local structural ordering in compositionally heterogeneous NMC oxides. (<i>on-schedule</i>)
Sept., 2019	Develop <i>in situ</i> techniques for studying surface reconstruction during synthesis of high-Ni NMC oxides. (<i>on-schedule</i>)
Sept., 2019	Complete structural/electrochemical characterization of the synthesized high-Ni NMC layered oxides. (<i>on schedule</i>)

Accomplishments: Studies of local cationic ordering during synthesis of $\text{LiNi}_{0.77}\text{Mn}_{0.13}\text{Co}_{0.10}\text{O}_2$



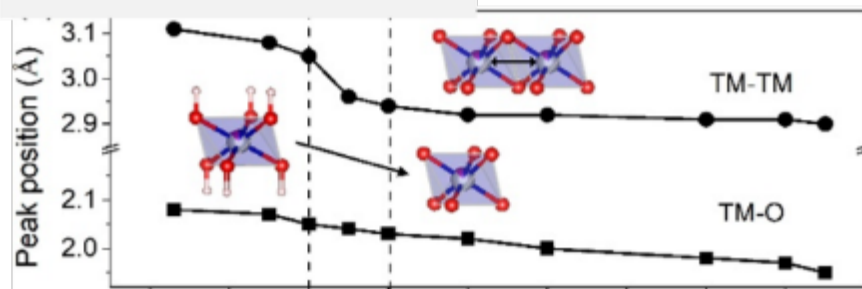
- **Details of the reaction process:** I) hydroxide \rightarrow II) intermediates towards the layered oxide (*driven by lithiation*) \rightarrow III) cationic ordering within layered framework.
- **Topotactic transformation:** with the layered framework retained throughout the synthesis process -- an advantage of using hydroxides as precursors.

Local ordering: *in situ* total scattering/pair distribution function (PDF)

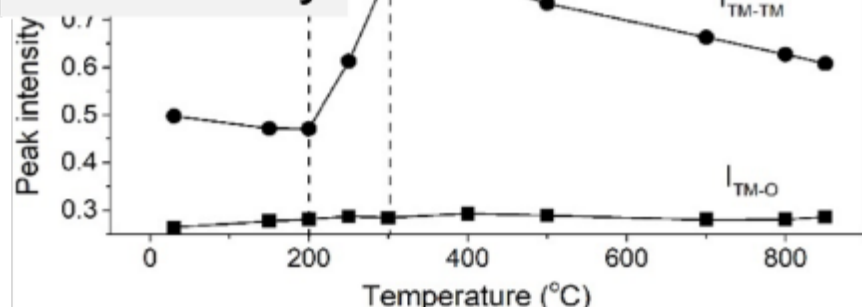


- Layered oxides (*ordering*)
- Intermediates (*highly disordered*)
- Hydroxides (*disordering*)

Inter-atomic distance



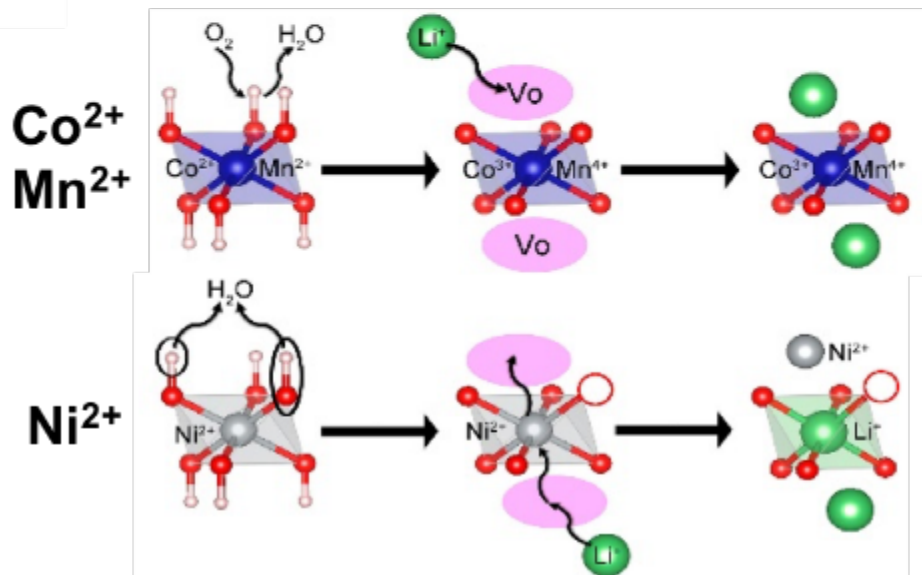
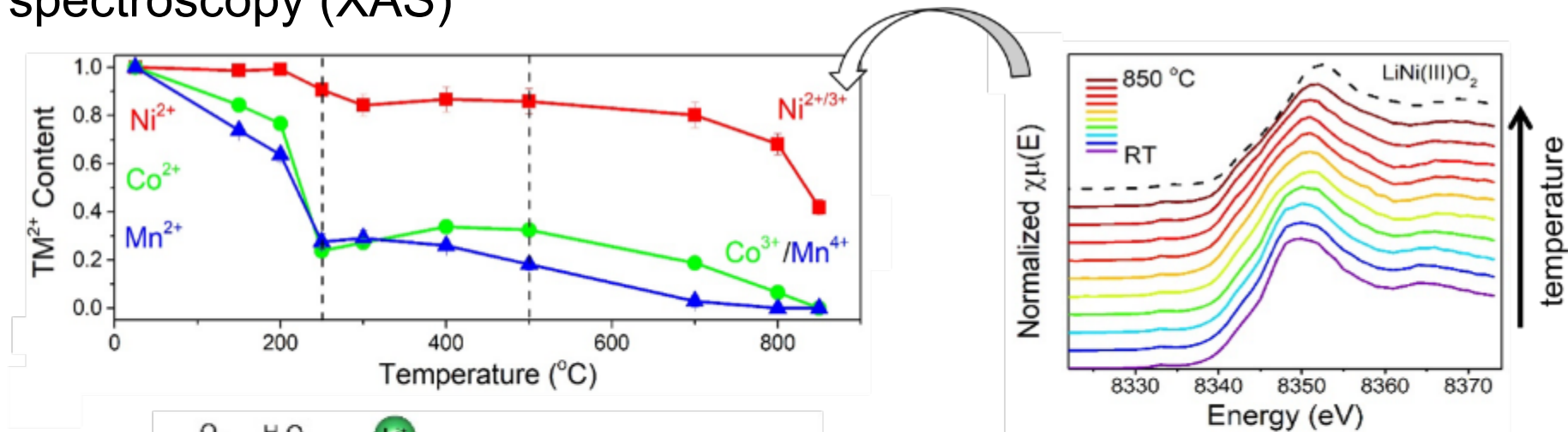
Atomic density



- Change in transition metal (TM)-O/TM-TM: oxidation/ordering of TMs.

- Local ordering (within TMO_6 octahedra): abrupt change, despite the overall small change in the bulk.

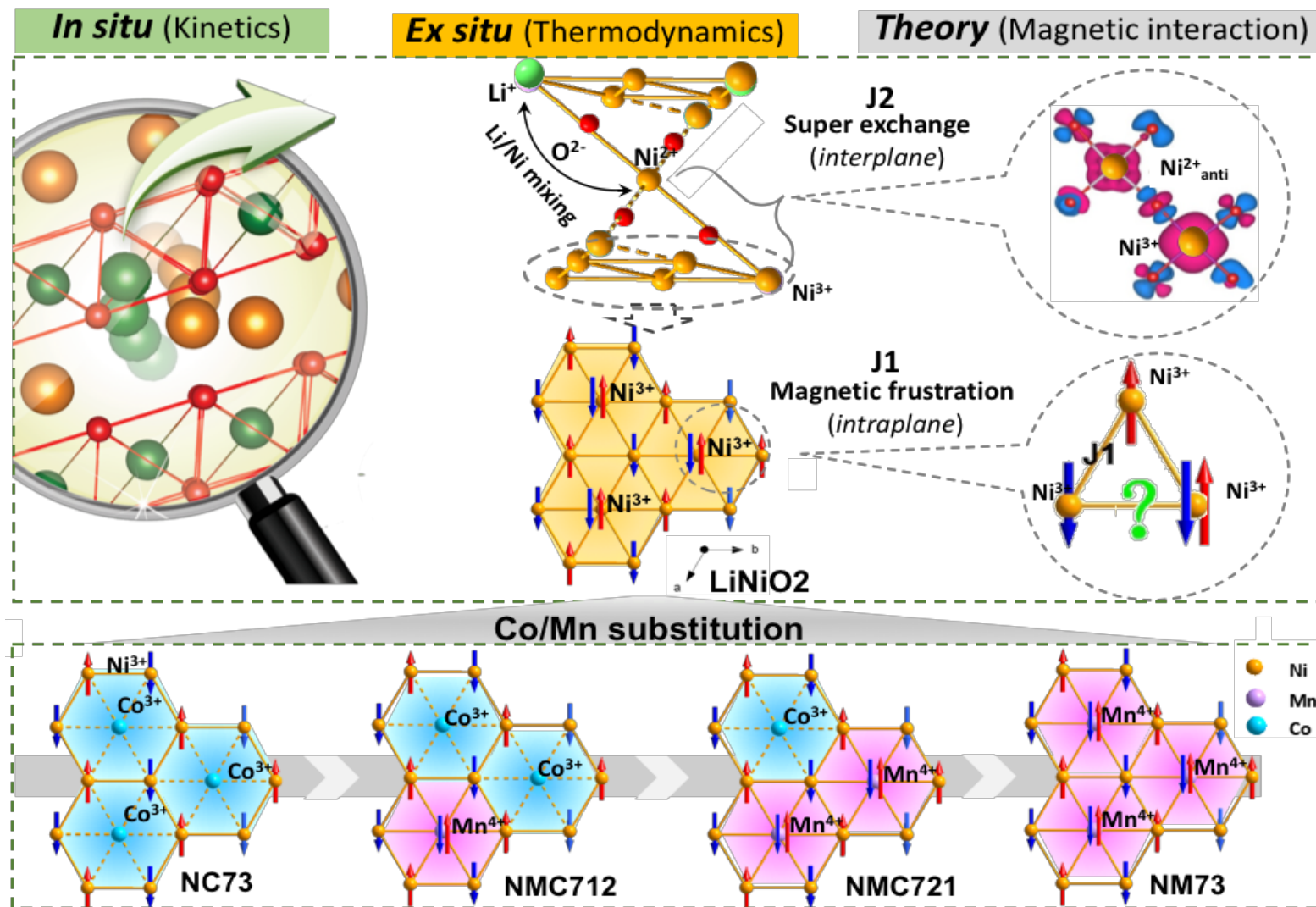
Preferential oxidation to Co/Mn over Ni: *in situ* X-ray absorption spectroscopy (XAS)



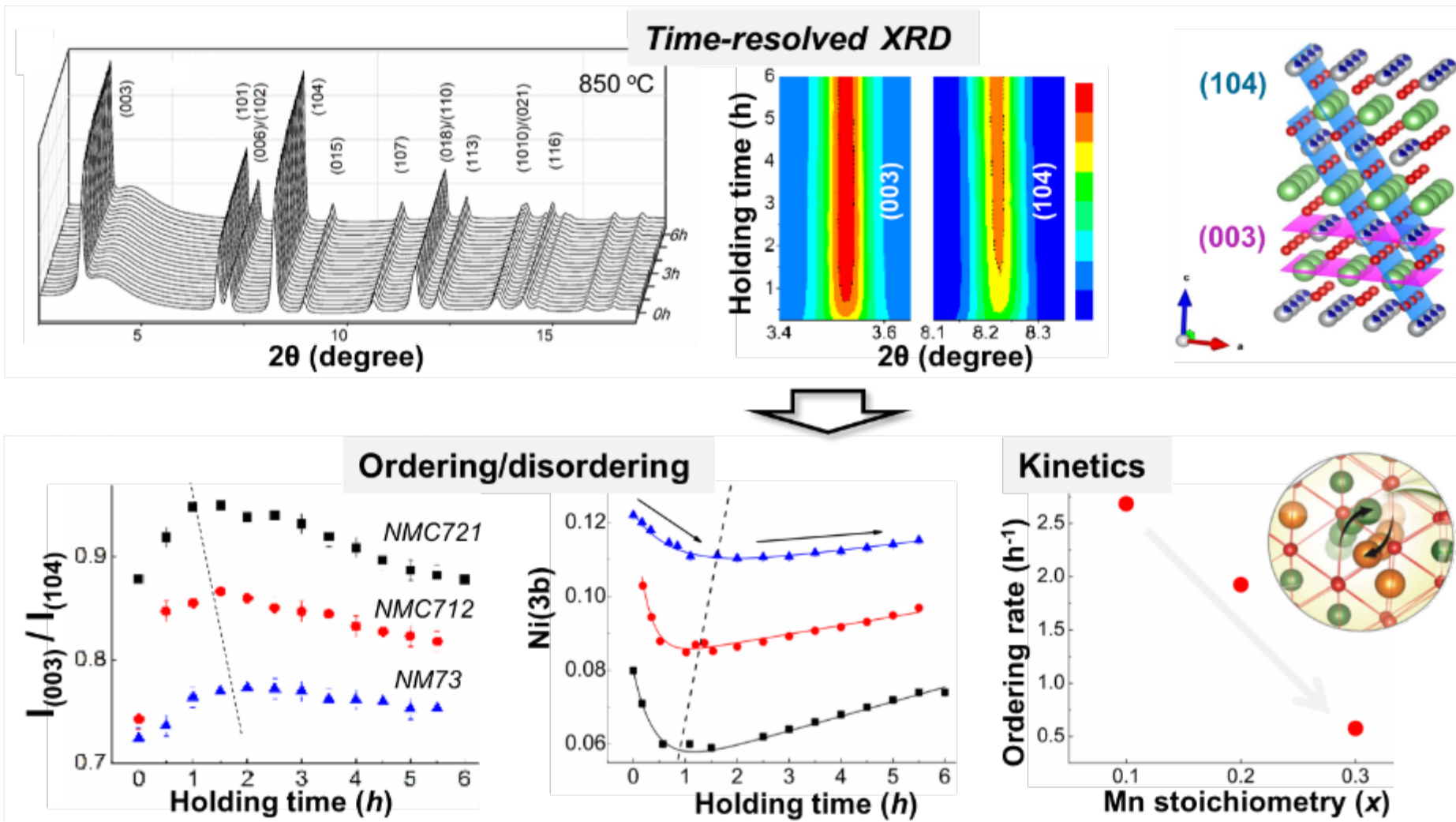
- **Cationic ordering:** coupled to the reconstruction of basic building units ($\text{TM}(\text{OH})_6 \rightarrow \text{TMO}_6$);
- **Li/Ni mixing:** due to formation of O-deficient NiO_6 , wherein Ni^{2+} is highly mobile and so tends to migrate to Li layer (See *backup slide 22 for details*).

➤ **Insight into synthetic design:** oxidation of Ni during synthesis is crucial to achieving high cationic ordering in high-Ni NMC.

Accomplishments: Identification of the role of Co/Mn substitution in tuning Li/Ni mixing in high-Ni NMC



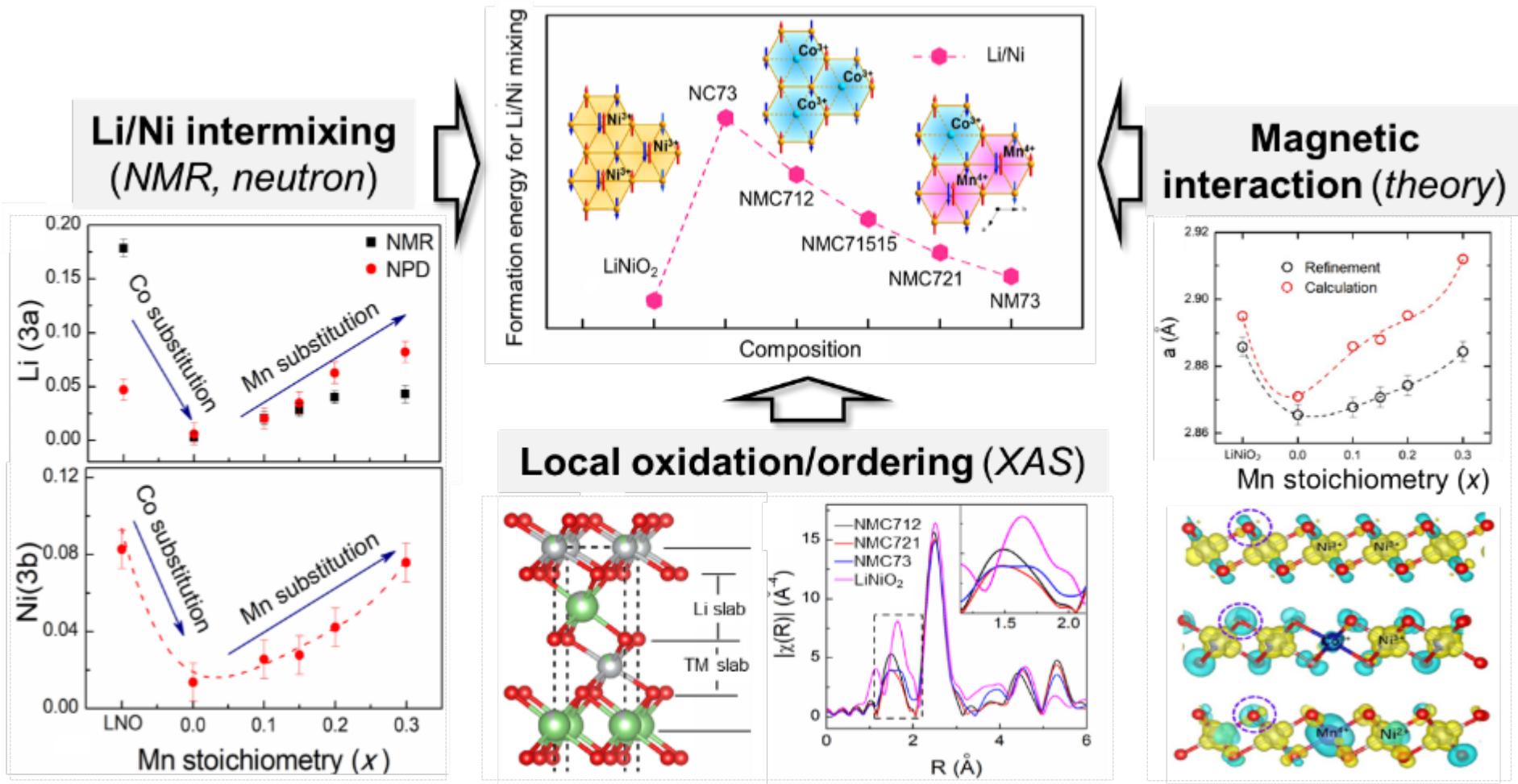
Kinetics of cationic ordering: *in situ* X-ray diffraction (XRD)



- **Role of Co/Mn substitution:** Co facilitates Li/Ni ordering; while Mn aggravates Li/Ni mixing and slows down the ordering kinetics.

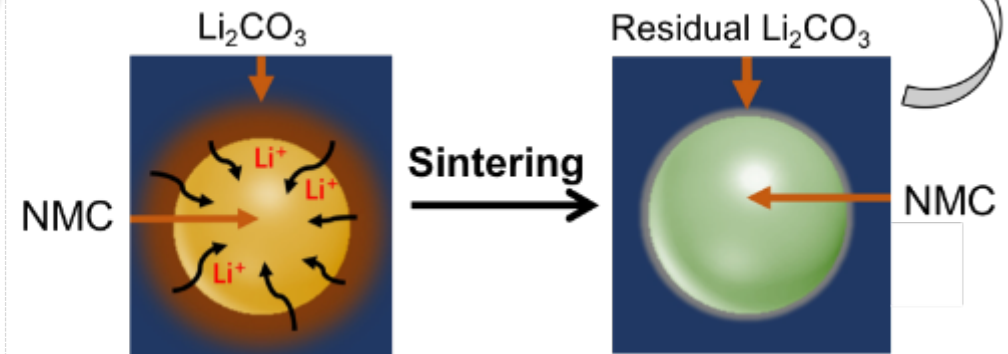
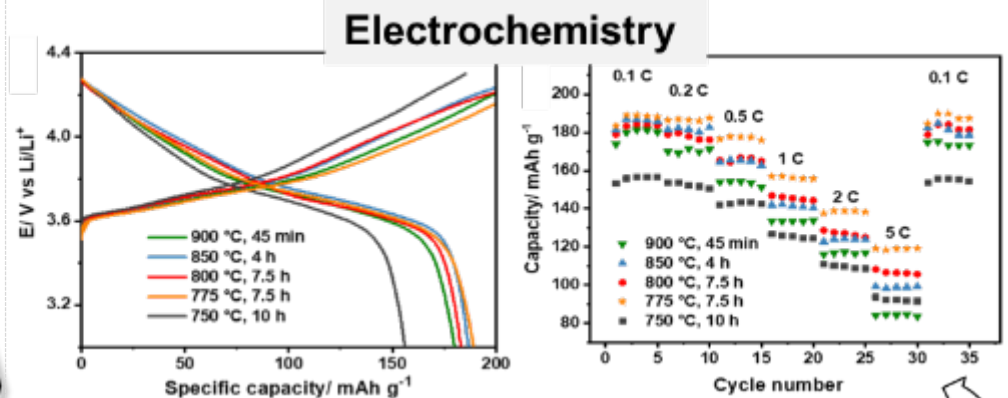
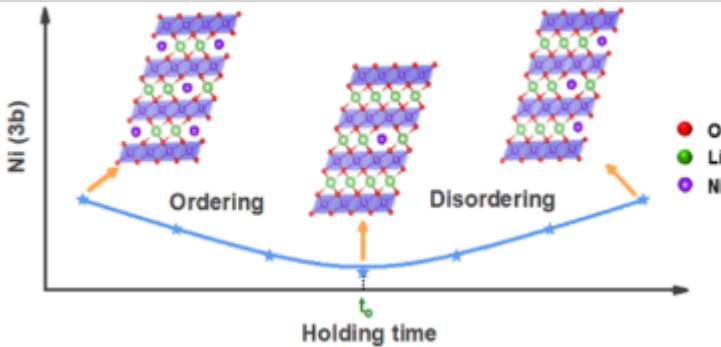
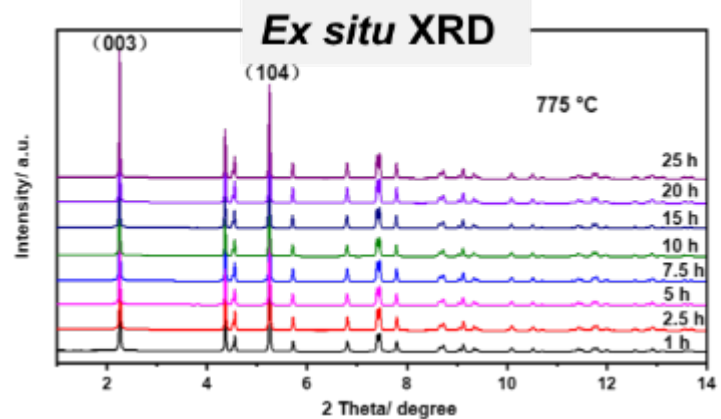
D. Wang et al., Chem. Mater. (in press; DOI: 10.1021/acs.chemmater.8b04673).

Thermodynamics of cationic ordering: NMR, NPD, XAS, theory



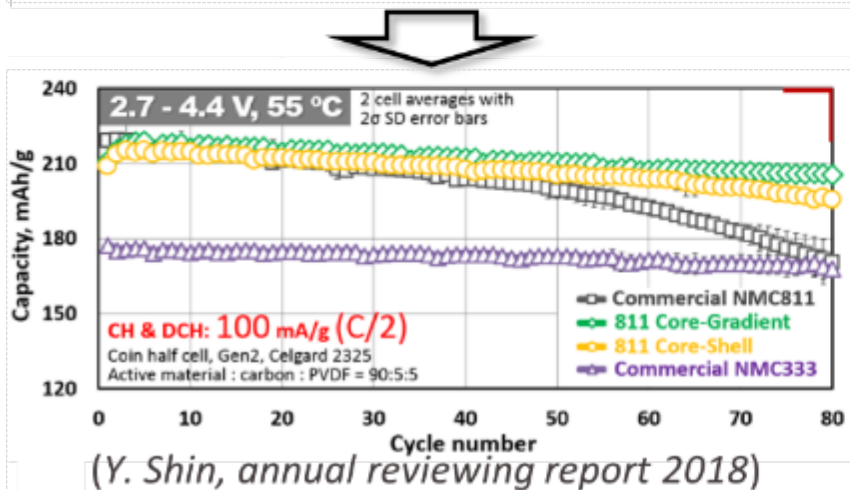
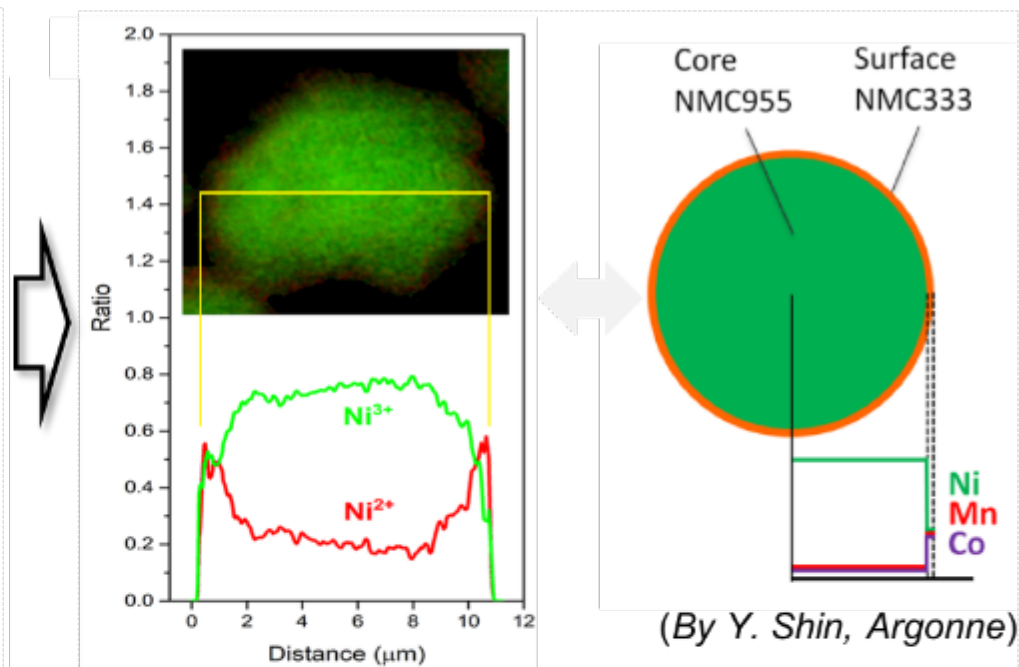
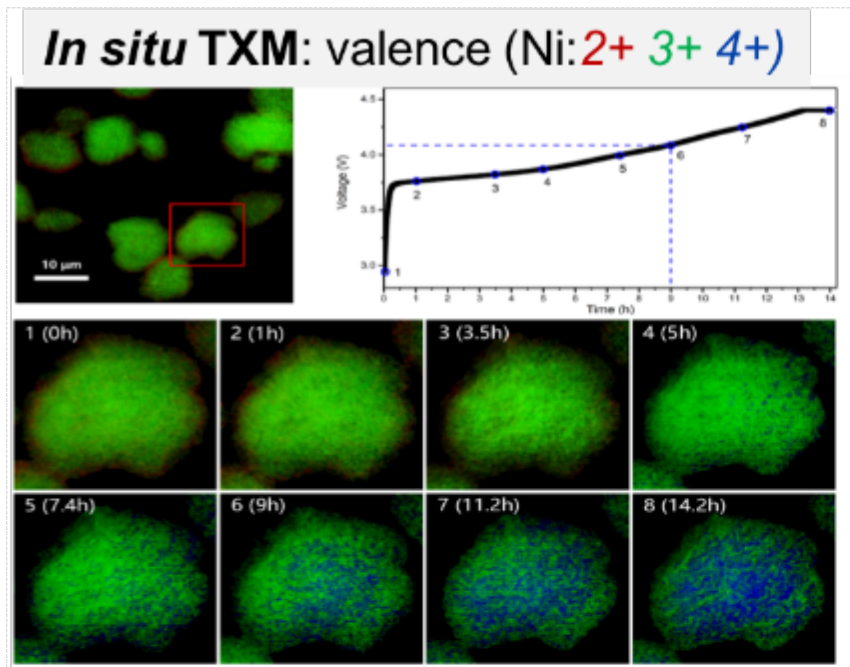
- Quantitative determination of Li/Ni mixing and direct comparison to theory:
- **Interplay between Li/Ni ordering and local magnetic interaction**, which needs to be considered in designing high-Ni NMC.

Accomplishments: Synthetic design of NMC71515 with controlled Li/Ni mixing



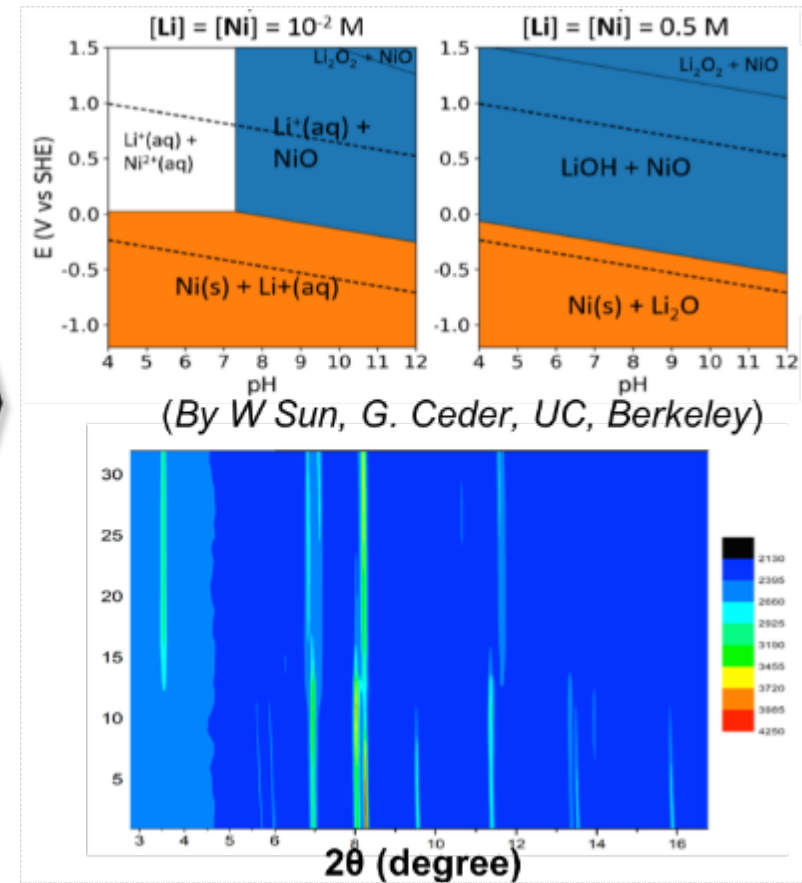
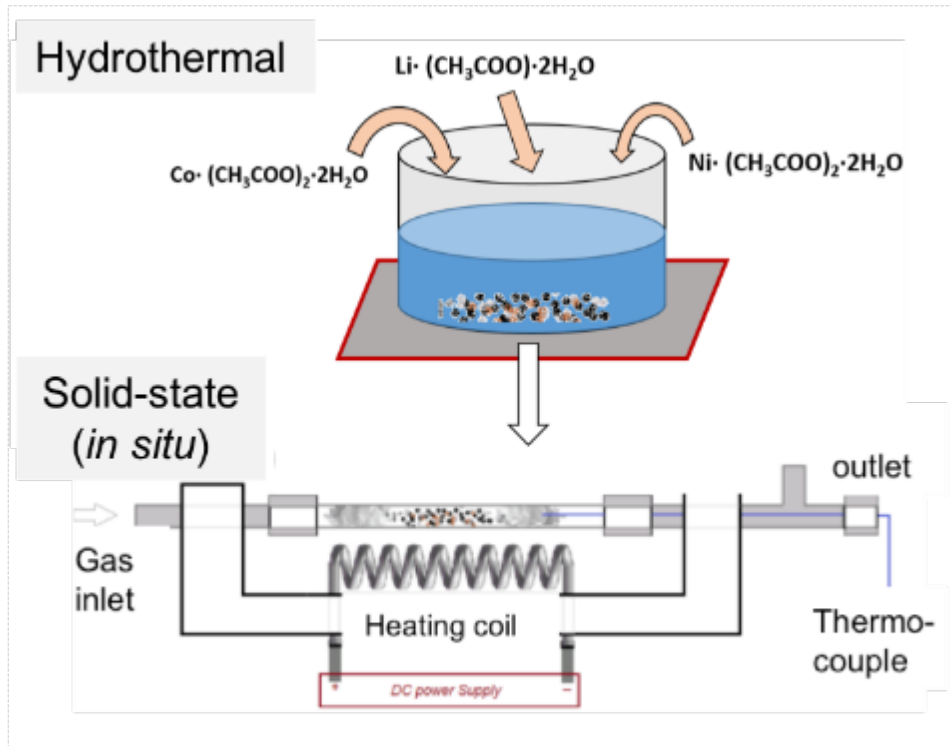
- Tuning Li/Ni mixing/electrochemical performance *via* temperature/time
 - enabled high capacity by minimizing Li/Ni mixing
 - large difference in rate capability: surface (*under investigation; Slide 23*)
- **Insights into synthetic route to controlling Li/Ni mixing and surface.**

Accomplishments: *In situ* characterization of local structural ordering in core-shell NMC811



- Established *in situ* X-ray techniques: probing local electrochemical redox with high spatial resolution;
- High cyclability: role of local chemical heterogeneity (➔ *insights into synthetic design of core-shell NMC; Slide 24*).

Accomplishments: Developing hydrothermal route to manipulating pathways of synthesizing layered NMC



- **Approach:** developed 2-step, hydrothermal + solid-state, procedures for controlling the synthesis process, coupled with theoretical and *in situ* studies;
- **Hydrothermal treatment:** an effective way of manipulating the kinetic pathways of forming layered oxides.

Response to Reviewers' Comments

We thank reviewers for their comments with great insights. Most of them are positive, so we only provide response to those ones with concerns.

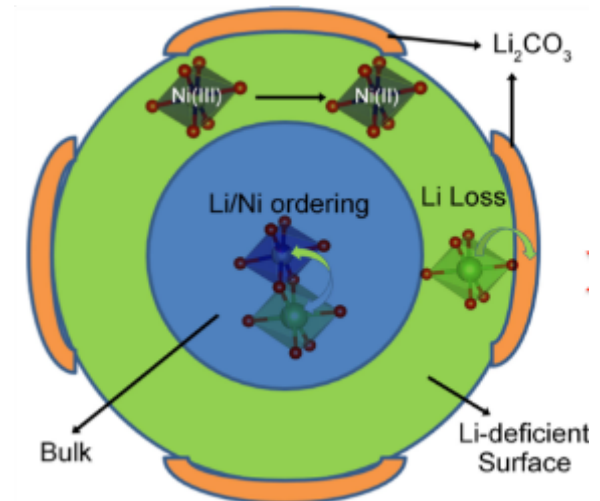
Comments	Response
One concern was raised on the resolution of X-ray techniques that may not be enough for probing surface states as those in core-shell/coated NMC811.	Some of the X-ray techniques have enough resolution for probing surface/interfaces (as demonstrated in Slides 4,13, 23, 24), and will be further developed for such studies.
One review recommended the project would benefit from comparison across different compositions of NMCs.	We have made investigation on a series of NMCs of different compositions (Slides 10-12), including NMC811 (Slide 13).
One reviewer noted that, besides study of solid-state synthesis from hydroxide precursors, synthesis from carbonates or in solvothermal processes would be equally valuable.	We already made investigation on solid-state synthesis using carbonates precursors, and solvothermal processes (Slide 15), and are putting more efforts on solvothermal synthesis.
Two reviewers suggested to expand the scope of this project to other battery areas.	We are very interested and will explore collaboration opportunities to expand the scope to new battery areas.

Collaborations

- **Brookhaven National Lab** (*L. Wu, Y. Zhu, A. Kiss, J. Thieme, K. Chen, M. Ge, X. Xiao, W-K. Lee, E. Dooryhee*)
 - Synchrotron techniques/capabilities for characterization of cathodes
 - Advanced electron microscopy imaging and spectroscopy of cathodes
- **Argonne National Lab** (*Z. Chen, K. Amine Y-H. Shin, Y. Ren, C. Sun, D. Abraham, V. Srinivasan*)
 - Synthesis and characterization of high-Ni NMC
 - Characterization of the materials from the Materials Engineering Research Facility (MERF)
 - Modeling of the synthesis
- **Lawrence Berkeley National Lab** (*W. Sun, G. Ceder*)
 - Theoretical prediction of the phases/ordering in high-Ni NMC
 - Characterization of cathode materials
- **Oak Ridge National Lab** (*J. Nanda, A. Huq*)
 - Neutron characterization of high-Ni NMC
- **Stony Brook U.** (*E. Takeuchi, K. Chen*)
 - Synthesis and characterization of high-capacity cathodes

Remaining Challenges and Barriers

- **Main barriers:** Capacity fading has been the main obstacle to realization of high-Ni NMCs with true commercial potential for lithium-ion batteries.
- **Technical challenges:** Synthesis of specific cathode materials by design has proven difficult due to the complexity of the reaction involved in chemical synthesis, and the high sensitivity of the phases, stoichiometry and morphology to synthesis parameters (*precursor, sintering temperature, atmosphere, heating/cooling rates...*)
 - Synthesis of high-Ni NMCs is even more challenging, due to the demanding requirement on the control of both cationic ordering in the bulk and surface/interfaces (*as illustrated*).



Future/On-going Work (*FY19-20*)

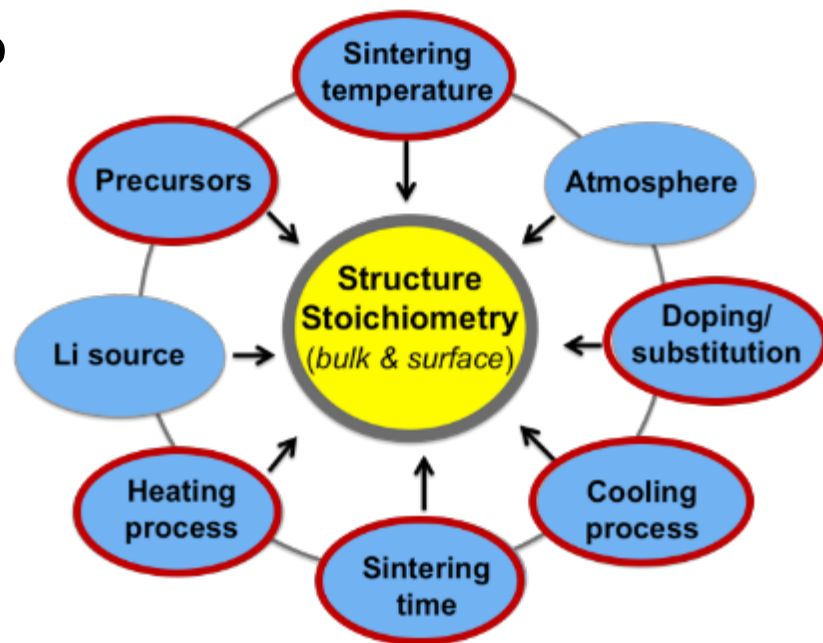
- Continue working on synthetic design of high-Ni NMC, with focuses on
 - impact of synthesis conditions on surface/interfaces and the electrochemical properties (See preliminary results in *Backup Slide 23*)
 - local cationic inter-diffusion/ordering in individual particles with compositional inhomogeneity (as demonstrated in *Backup Slide 24*)
- Develop new *in situ* techniques and capabilities, specialized for probing synthesis reaction under real conditions
 - simultaneous or combined X-ray scattering/spectroscopy/imaging for multimodal characterization
 - techniques capable of high spatial resolution and/or high sensitivity to local structural ordering at surface/interfaces
- Apply the established approaches to synthetic design of
 - NMC811 and those with higher Ni content
 - low-Co/Co-free cathode materials

Any proposed future work is subject to change based on funding levels

Summary

We have established approaches for synthesis of cathode materials by design.

- **Relevance:** Develop synthesis protocols for preparing low-cost, high energy density cathodes with potential application in electric vehicles.
- **Approaches:** *In situ* techniques/capabilities are developed for *real time* probing synthesis reaction during preparation of cathode materials.
- **Technical Accomplishments:**
Extensive investigation has been made to the impact of synthesis parameters (*as highlighted in red*) on the structure and stoichiometry in high-Ni NMC.
- **Collaborative Research:** Extensive collaboration was established on synthesis/characterization of cathodes.
- **Future Work:** Apply the established approaches to synthetic design of high-Ni NMC and other types of battery materials.



Acknowledgement

- Support from Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.
- Contribution by team members and collaborators

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YoungHo Shin

Yang Ren

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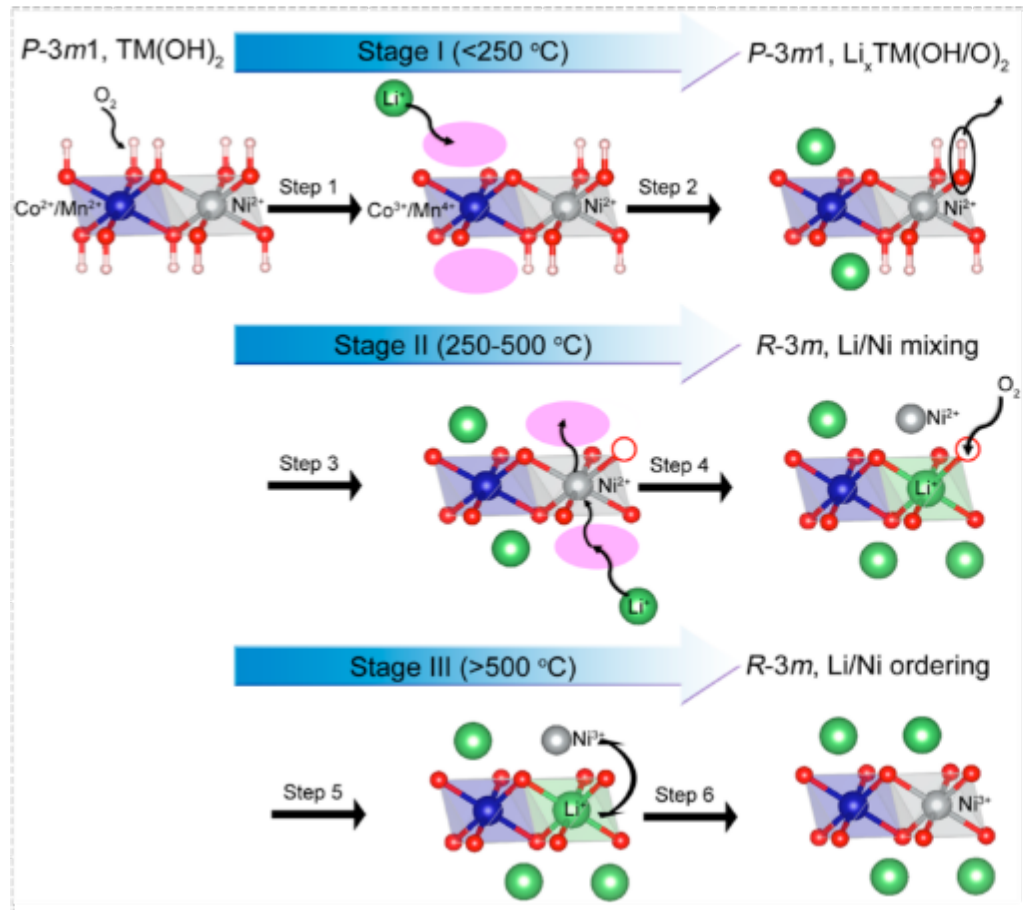
Gerbrand Ceder

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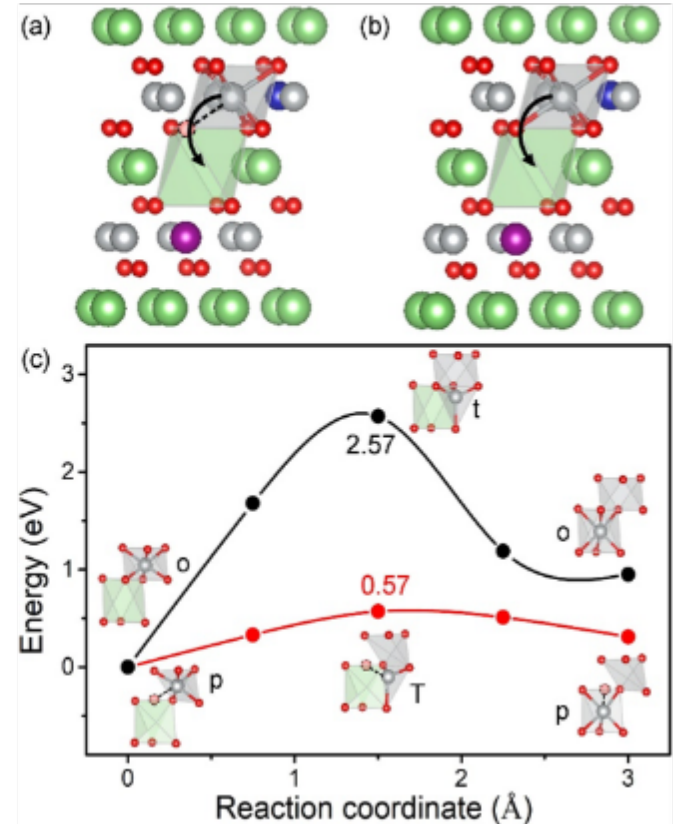
Ashfia Huq

Technical Backup Slides

Backup (1) Li/Ni mixing due to O-deficiency in NiO₆

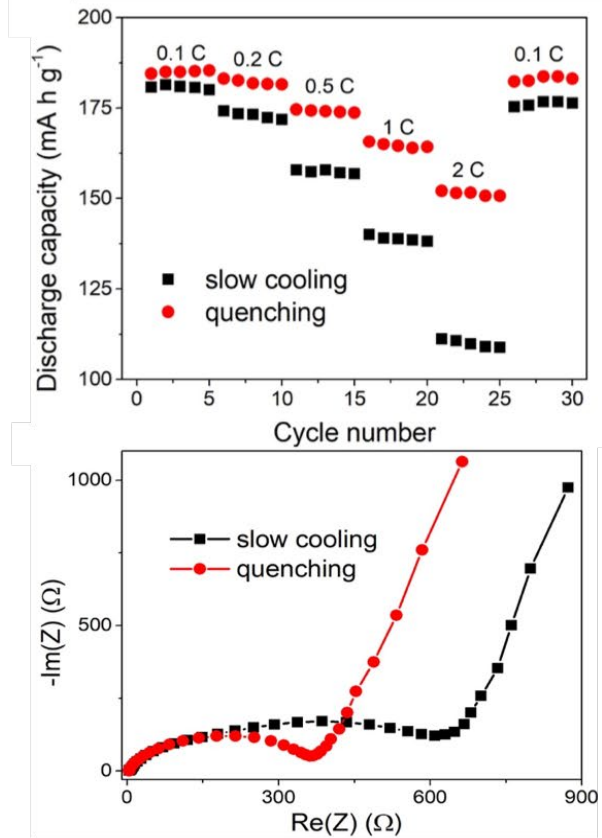
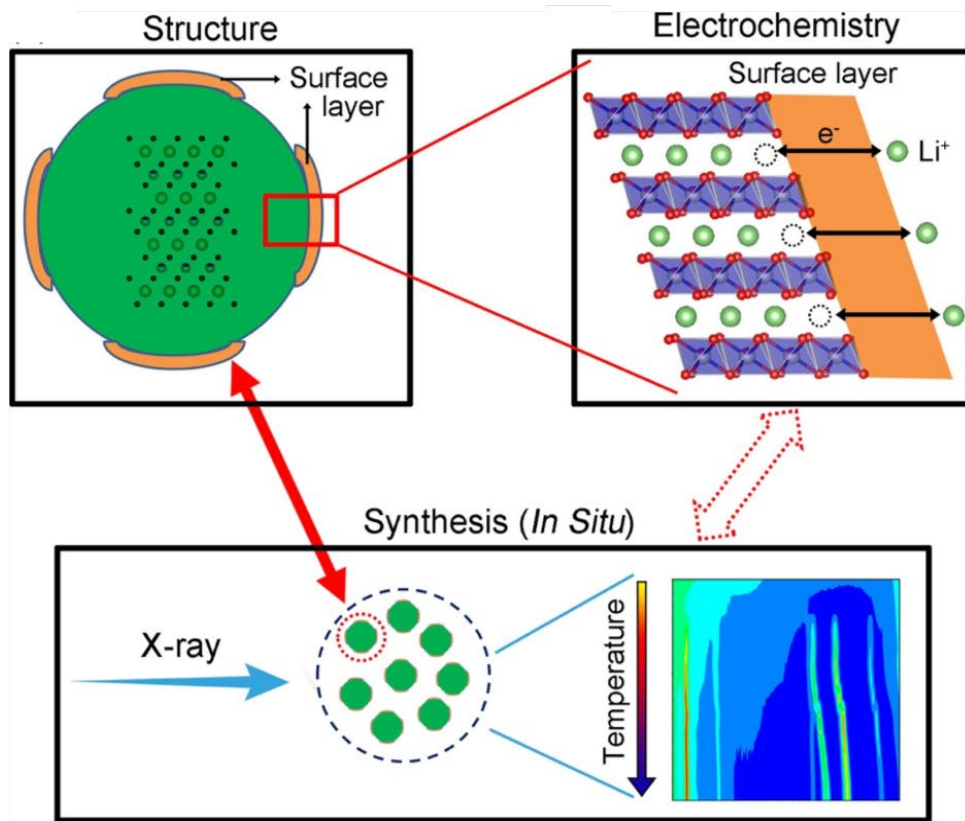


Energy barriers for Ni migration:



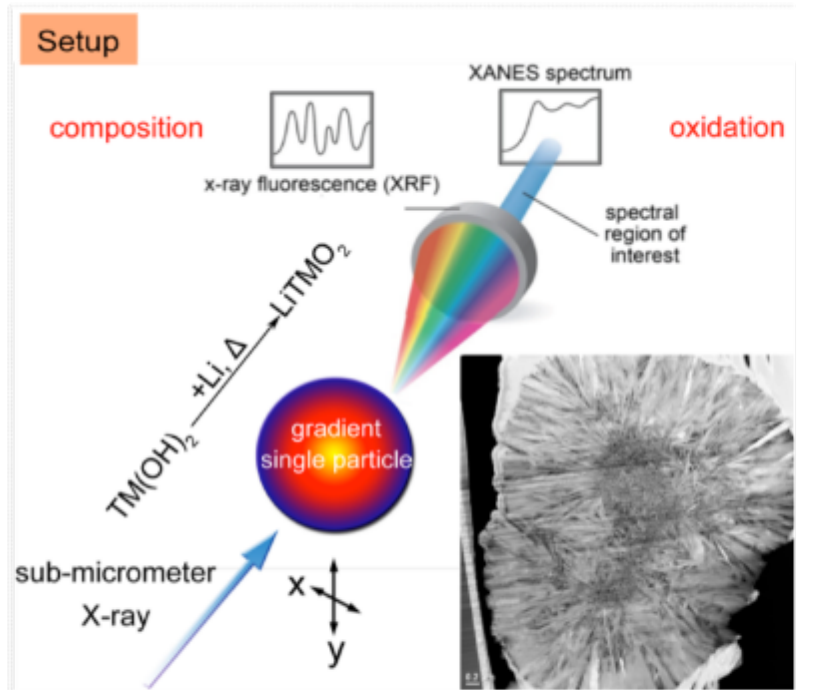
- **High Ni diffusivity induced by oxygen deficiency in NiO₆**
 - In the the oxygen-deficient NiO_{6-x}: the activation energy for Ni migration is low, only 0.57 eV -- comparable to that for Li⁺ migration.

Backup (2) Cooling rate-dependent surface change during synthesis of high-Ni NMC

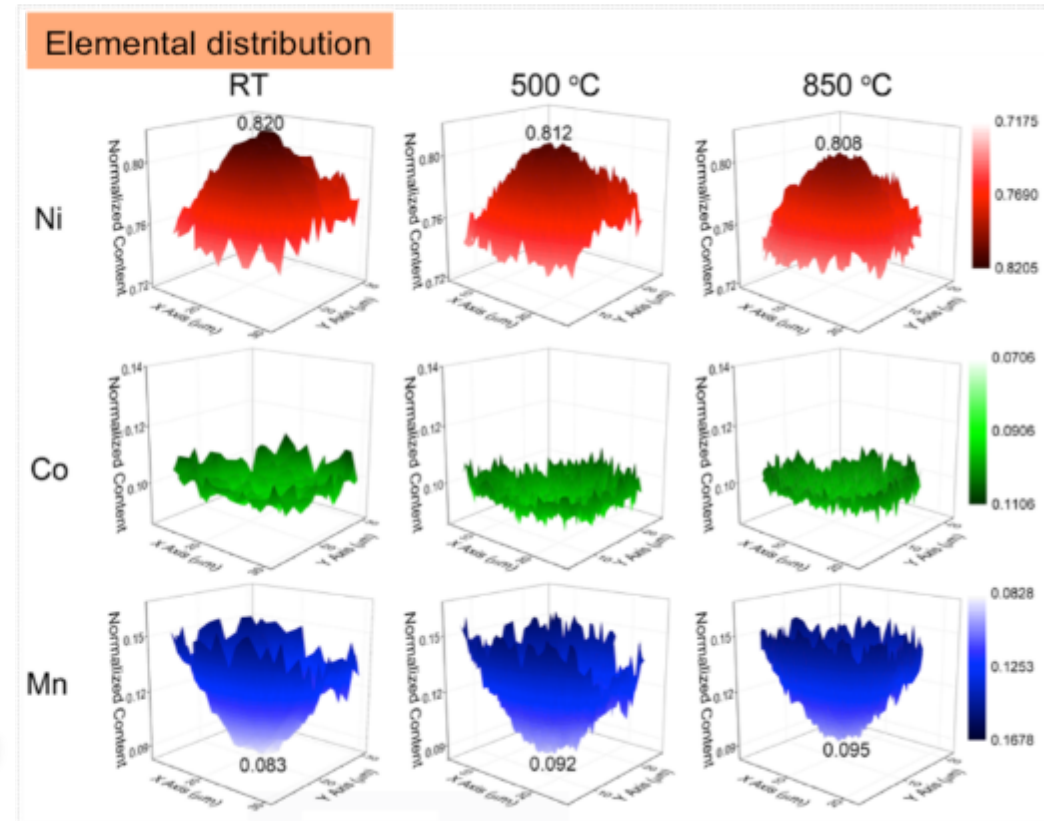


- Rate capability is much enhanced by quenching (compared to slow cooling), likely due to the improved surface properties, and so the reduced impedance to Li intercalation;
- **Future work:** *In situ* studies on the impact of cooling on surface properties.

Backup (3) *In situ* probing of inter-diffusion in high-Ni NMC during synthesis



✧ Setup for *in-situ* X-ray spectro-imaging of a single particle during synthesis



- Quantification of elemental inter-diffusion within a single particle
 - Fast inter-diffusion < 500 °C, comparable to that at high temperatures.